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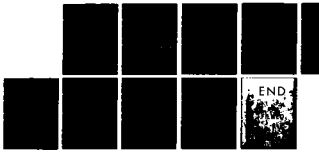

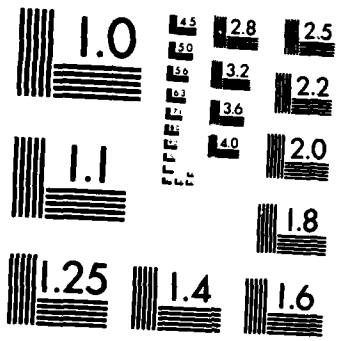

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Kai-Shue Lam, Michael Hutchinson and Thomas F. George

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LASER-INDUCED BOUND STATES AT SURFACES: ION NEUTRALIZATION AND ADSORPTION

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Abstract A laser can be used to generate bound states, both electronic and vibrational, of a foreign atom on a solid surface, and is capable of enhancing processes like ion neutralization and adsorption.

INTRODUCTION

Two mechanisms for laser-generated bound states of a foreign species on a solid surface are discussed. The first, ion neutralization, leads to a bound electronic valence state of a projectile ion that is not degenerate with any electronic band states of the surface, while the second, radiative adsorption, gives a stable vibrational state of an adsorbed atom. The laser intensity plays the dominant role in the first process, whereas in the second a resonantly-tuned frequency is of greater importance.

ION NEUTRALIZATION

In many theories treating neutralization of ions scattered from solid surfaces,[1,2] resonance processes play a dominant role. This kind of resonance is between a discrete state and a continuum level. Thus a valence level of the

projectile ion (the discrete state) is considered to have a position-dependent energy $\epsilon_0(z)$ (see Fig. 1) which, at some region of small z, is resonant with a continuum of band levels of the electronic states in the solid surface; the position z represents some measure of the distance of the ion from the surface. The bound-continuum interaction is usually assumed to be significant only for small z, that is, when the ion is near the surface. Moreover, the strength of the interaction is assumed to be such that both the shift and width of the resonant state are small, and that the energy spectrum of the ion-surface system is the same as that of the band states of the solid surface. These limitations on the bound-continuum interaction, together with the particular nature of the model--one discrete state embedded in one continuum--lead to the situation where true bound states of the ion-surface system play no role at all in the discription of the mechanisms leading to charge transfer. If such mechanisms require true bound states, they have to be added to the model. For example, Auger neutralization may take place if a deep-lying unoccupied level of the incoming ion is available.[3]

Within the constraints of the model described above and a particular physical system, the bound-continuum interaction has a fixed strength, and thus true bound states either enter the picture or not at all. With the introduction of a laser, however, the situation is changed drastically. The fact of crucial importance is that both the laser frequency and the field strength are adjustable. Thus the same model, when it is understood that the bound-continuum interaction is due to a field coupling, can not only incorporate a variable $\epsilon_0(z)$ (variable not only with respect to z but by amounts directly related to $\hbar\omega$) but also a variable coupling strength

(directly related to the field strength). It is precisely these variable quantities which lead to the possible existence of true bound states, even when they are precluded in the absence of the field. The laser may then be used to enhance bound state mechanisms which are either unimportant or impossible in the field-free situation. With respect to the Auger neutralization process mentioned above, the laser may literally create a "deep-lying" valence state to act as receptor of an electron from a band level. Such a state may also interact resonantly with any core levels of the solid surface that happen to be approximately degenerate with it. In what follows we give a brief discussion of the theory behind the formation of the laser-induced bound state.

The schematic picture of the energy level structure in our model is given in Fig. 1. The Hamiltonian may be written as

$$H(z) = \sum_k \varepsilon_k n_k + (\varepsilon_0(z) + \hbar\omega) n_0 + \sum_k [V_k(z) c_0^\dagger c_k + \text{h.c.}], \quad (1)$$

where $V_k(z)$ is the bound-continuum interaction provided by the field coupling, and k is the band index. The emergence of possible bound states is most easily seen by focusing on the eigenvalue equation for H(z):

$$\varepsilon - (\varepsilon_0 + \hbar\omega) + g^2 \int d\varepsilon' \frac{\rho(\varepsilon') |V(\varepsilon')|^2}{\varepsilon' - \varepsilon} = 0, \quad (2)$$

where we have introduced a coupling strength g into $V_k(z)$ such that

$$V_k(z) = gV(\varepsilon), \quad (3)$$

and the z dependence is not explicitly written on the RHS. For radiative coupling, g^2 is directly proportional to the field strength.

Under what conditions will a true bound state emerge? There will be bound states when Eq. (2) admits negative

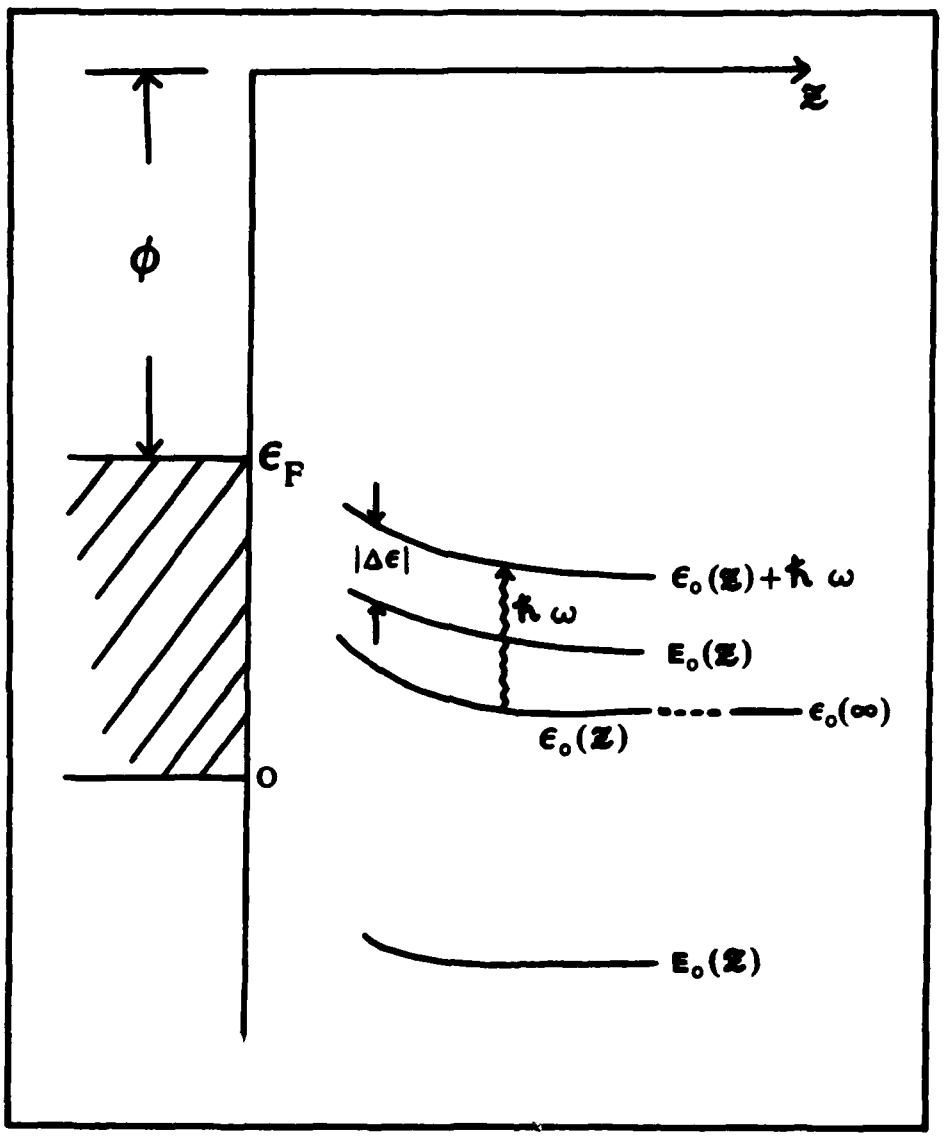

FIGURE 1. Energy level structure of the model describing ion neutralization at a solid surface. $\epsilon_0(z)$ is the unoccupied valence level of the ion, ω is the laser frequency, and $\Delta\epsilon$ is the level shift (this is shown to be negative in the picture). $E_0(z)$ is either a virtual level when it is degenerate with the conduction band, or a true bound state when it is outside the conduction band. ϵ_F is the Fermi energy, and ϕ is the work function.

energy solutions. Let this solution be $E_0 = -x$, where $x>0$. Eq. (2) then reads

$$x + \varepsilon_0 + \hbar\omega = g^2 \int d\varepsilon' \frac{\rho(\varepsilon')|V(\varepsilon')|^2}{\varepsilon' + x} . \tag{4}$$

Examination of the quantitative picture for a graphical solution quickly reveals that there will be a negative energy solution only when

$$g > g_{crit},$$

where

$$g_{crit} = \left[\frac{\varepsilon_0 + \hbar\omega}{\int d\varepsilon' \frac{\rho(\varepsilon')|V(\varepsilon')|^2}{\varepsilon'}} \right]^{1/2} . \tag{5}$$

Thus whenever the laser field strength is increased beyond a value specified by the critical coupling constant g_{crit}, a true bound state emerges. Furthermore, the model only admits one and only one such state.

For $g < g_{crit}$, however, the valence level of the projectile ion becomes an unstable (virtual) state with a shift in energy, $\Delta\varepsilon$, given by

$$\Delta\varepsilon = -g^2 P \int d\varepsilon' \frac{\rho(\varepsilon')|V(\varepsilon')|^2}{\varepsilon' - E_0} , \tag{6}$$

where P denotes the principal value of the integral. Eq. (6) implies that when

$$|\Delta\varepsilon| > \varepsilon_0 + \hbar\omega,$$

we have a true bound state. Looking at Fig. 1, then, the laser can be imagined to do the following thing: As the field strength is increased, the resonant valence level $\varepsilon_0 + \hbar\omega$ is pulled progressively down the conduction band. As long as $g < g_{crit}$, $E_0(z)$ stays within the conduction band, and at most we have an unstable state. But when

$g > g_{crit}$, $E_0(z)$ falls outside of the band, and a true bound state results.

RADIATION-ASSISTED ADSORPTION

We now consider an alternative mechanism for laser-generated bound states. This is the process of radiative adsorption, which is illustrated in Fig. 2. During the encounter with a surface, an adatom can undergo transition to a bound state of the adatom-surface potential by stimulated emission of a photon. If the surface were rigid, such a bound state would be unstable to the reverse process, photon absorption. However, by coupling the adatom motion to the phonon "bath" of the solid, there exists the possibility of a simultaneous decay to a lower-lying bound state by phonon creation. Such a state would be a true final state, except at temperatures sufficiently high that phonon annihilation (feedback) is important.

We shall now sketch the theory of this process for adsorption on a one-dimensional lattice (the extension to three dimensions is straightforward, but the notation for the one-dimensional problem is simpler). We may write the Hamiltonian as

$$H = H_0 + H^r_{int} + H^p_{int}, \tag{7}$$

where

$$H_0 = H^r + H^p + H^a, \tag{8}$$

and the superscripts r, p and a stand for the radiation, phonons and the adatom, respectively. The corresponding eigenvectors of these zeroth-order Hamiltonians are written

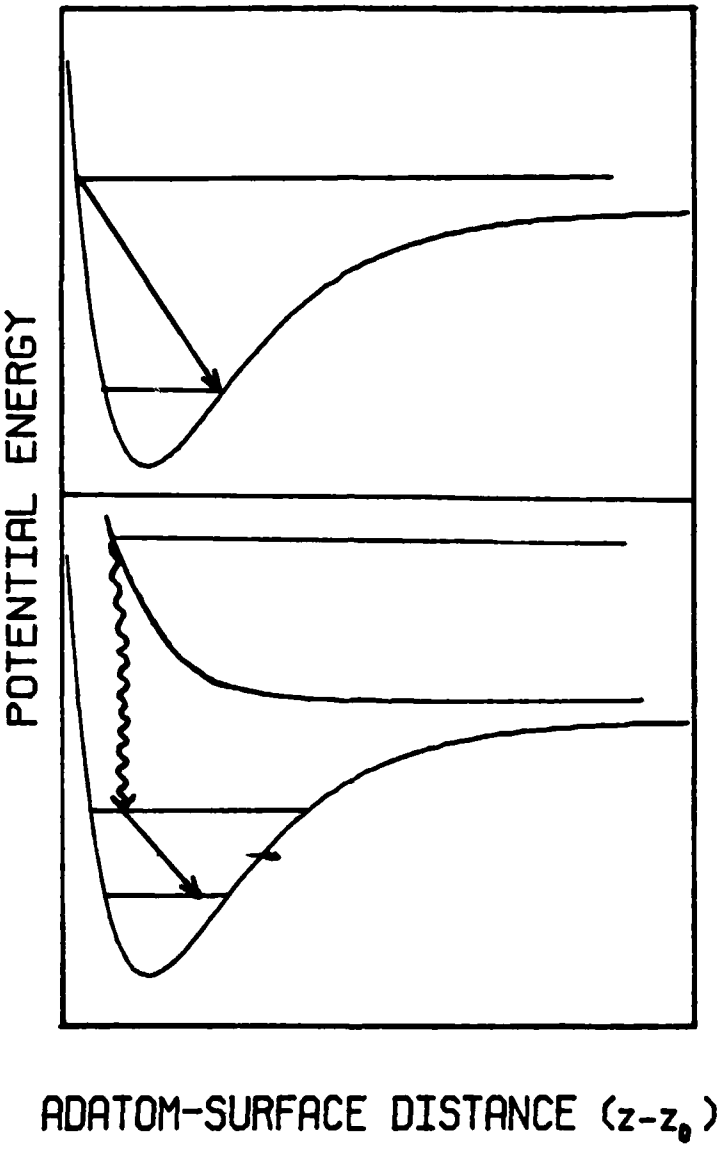

FIGURE 2. Adsorption events depicted in the space of the atom-surface electronic eigenstates. Top: adsorption from a continuum by the creation of a single phonon. Bottom: adsorption from a continuum by the "simultaneous" creation of a photon and a phonon. The phonon events are depicted by straight arrows.

as $|n^r_{k\sigma}>, |n^p_k>$ and $|E^+>, |f>$. The third and fourth eigenvectors (of H^a) are, respectively, the scattering state at energy E (with an outgoing wave boundary condition) and a final bound state f. The latter state thus represents the adatom bound to the surface. Using a projection operator Q to project out the bound intermediate state $|m>$ to which the radiative transition is made, it is now possible to write the adsorption rate R due to a plane-polarized laser as

$$R = |<n^p_k+1|<f|H^p_{int}|m>|n^p_k>|^2$$

$$\times |(G^+_{QQ})_{mm}<n^r_{k0}+1|<m|H^r_{int}|E^+>|n^r_{k0}>|^2$$

$$\times \delta((E-E_f) - \hbar\omega_p - \hbar\omega_r) , \qquad (9)$$

where

$$G^+_{QQ} = \lim_{\varepsilon\to 0} (E + i\eta - H_{QQ} - H_{QP}G^+_0 H_{PQ})^{-1}, \qquad (10)$$

$$P = 1-Q$$

and

$$O_{XY} = XOY .$$

G^+_0 is the Green's function for non-resonant scattering and is expanded in a product basis of surface plane waves and adatom scattering out-waves.

We now consider the contribution of a single-phonon transition to the rate by expanding the operator H^p_{int} in a Taylor's series in the lattice coordinate z_ℓ:

$$H^p_{int} = \sum_\ell d^\ell(z) (z_\ell - z^0_\ell), \qquad (11)$$

where z is the corrdina : of the as atom, and z^0_ℓ is the equilibrium (frozen latti·· coordinate of atom ℓ in the

chain,

$$d^{\ell}(z) = \frac{\partial}{\partial z_{\ell}} V(z-z_{\ell})\Big|_{z_{\ell}=z_{\ell}^{0}} . \tag{12}$$

To arrive at the total averaged rate $\langle R \rangle$, it is necessary to average over initial and sum over final phonon states. Dropping for simplicity the Fock states of the radiation field, we are led by standard manipulations[4,5] to

$$\langle R \rangle = \sum_{\ell} \frac{|\langle f|\sum_{\ell} d^{\ell}(z)|m\rangle|^2}{NM} \frac{1}{\omega_p} (\bar{n}_p + 1)\, \rho(\omega_p)$$

$$\times\ |(G^{+}_{QQ})_{mm}\ \langle m|H^{r}_{int}|E^{+}\rangle|^2 , \tag{13}$$

where $\rho(\omega_p)$ is the phonon density of states as a function of the energy-conserving frequency, ω_p, $\bar{n}_p$ is the average occupation number of phonon mode p,

$$\bar{n}_p = (e^{\hbar\omega_p/kT}-1)^{-1},$$

and there are N atoms in the chain, each of mass M. An important feature of Eq. (13) is the natural separation of the gas-phase problem from that of the surface. The only point of contact is in $(G^{+}_{QQ})_{mm}$, which would contain width and level shift terms due to the phonons, and related terms which are due to the radiative interaction.

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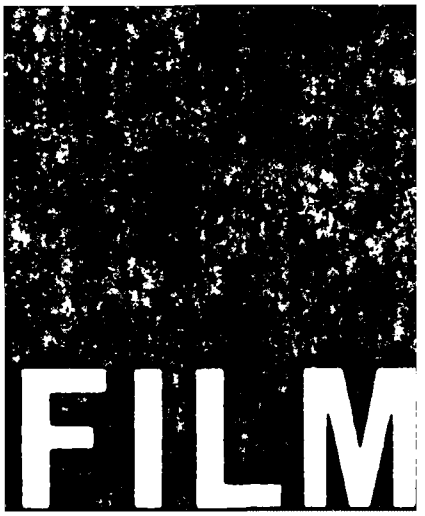
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